

Fermilab

Fermi National Accelerator Laboratory
P.O. Box 500 • Batavia, Illinois • 60510

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pH and resistivity of the BCP mix diluted in UPW

C. Boffo, D. Connolly, D. Hicks, J. Hoffman

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1. Introduction

Etching plays an important role in the production of superconducting cavities (SRF) [1]. As other laboratories engaged in RF superconductivity R&D did, FNAL is also developing a facility for the chemical etching of niobium (Nb) cavities.

Two techniques are commonly accepted for cavity etching:

- Chemical etching – buffered chemical polishing (BCP)
- Electropolishing (EP)

Among them, at FNAL it was decided to pursue chemical etching, which is considered a reliable technique tested by several labs for many years [2]. In the past, numerous mixtures of acids have been tested leading to the actual buffered chemical polishing mix (BCP) characterized by the following composition by volume:

| | | | | | |
|---|----|--------------------------------|------|-----|-----|
| 1 | of | HF | 49 | %wt | [3] |
| 1 | of | HNO ₃ | 69.5 | %wt | [4] |
| 2 | of | H ₃ PO ₄ | 85 | %wt | [5] |

Because of the dangerous nature of the chemicals involved, safety considerations require the development of a proper process and a truthful control algorithm. For the post-processing rinsing of the cavities, one needs to know the expected pH of the water used to rinse the cavity. On the other hand, for early detection of leaks in the hydraulic system, which is done by measuring the conductivity of the rinsing water used in the process, one needs to understand the relationship between pH and resistivity of the diluted BCP mix. This note is an attempt to address these issues.

2. BCP Properties

The BCP mix can be purchased pre-mixed in 55 gallon barrels or it can be prepared starting with the three acids. For the new facility it is planned to use the premixed solution, but for now, given the small quantities handled (less than 1 gallon) all the etching is performed using BCP mixed in house. The information on the acids needed to calculate the pH is listed below:

| | HF 49%wt | HNO ₃ 69.5%wt | H ₃ PO ₄ 85%wt |
|---|--------------------|--------------------------|--------------------------------------|
| Molecular weight PM | 20 | 63 | 98 |
| Density [g/ml] D | 1.000 | 1.408 | 1.690 |
| Equilibrium const. K_a | 4*10 ⁻⁴ | ∞ | 7.5*10 ⁻³ * |

* Only the dissociation of the first hydrogen ion is considered for this polyprotic acid

Table 1 Acid properties

Using this data it is possible to calculate the molarity (M) of each acid solution through the relationship:

$$M = \frac{10D * \% wt}{PM} \quad (1)$$

Leading to the following result:

| | | |
|--------------------------------|----|---------|
| HF | -> | 24.50 M |
| HNO ₃ | -> | 15.53 M |
| H ₃ PO ₄ | -> | 14.66 M |

These 3 solutions are mixed in 1:1:2 volume proportion giving the following molar concentration of each acid in the mix:

| | | |
|--------------------------------|----|--------|
| HF | -> | 6.13 M |
| HNO ₃ | -> | 3.88 M |
| H ₃ PO ₄ | -> | 7.33 M |

Now it is possible to calculate the correct hydrogen ions (H⁺) concentration in the mixed solution.

3. Hydrogen ions concentration

Since nitric acid is by far the strongest of the four species in solution (3 acids and ultra pure water UPW), in first approximation, it is possible to calculate the pH of the mix directly from its concentration. Nitric, being a strong acid, completely dissociates in UPW with the result that the concentration of H⁺ equals the initial acid concentration.

However when the acid molar concentration falls below 10⁻⁴, one cannot ignore the UPW dissociation and the effect of the other two acids without committing considerable errors. It is also feasible to consider the sum of the separate contributions of the acids and UPW to the H⁺ concentration, although, since the three values are mutually affected, the most accurate method is to explicitly solve the equilibrium, the mass and the charge equations for the mix.

Equilibrium equations:

$$K_{HNO_3} = \infty \quad (2)$$

$$K_{HF} = \frac{[H^+][F^-]}{[HF]} \quad (3)$$

$$K_{H_3PO_4} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \quad (4)$$

$$K_w = [H^+][OH^-] \quad (5)$$

Where the molar concentration of each species is considered in square brackets and K_w (10^{-14}) is the constant of dissociation for UPW.

Mass conservation equations:

$$M_{HNO_3}^0 = [NO_3^-] \quad (6)$$

$$M_{HF}^0 = [HF] + [F^-] \quad (7)$$

$$M_{H_3PO_4}^0 = [H_3PO_4] + [H_2PO_4^-] \quad (8)$$

Where M^0 is the initial molar concentration of each species.

Charge conservation equation:

$$[H^+] = [NO_3^-] + [F^-] + [H_2PO_4^-] + [OH^-] \quad (9)$$

Solving the system of these 8 equations one can find the H^+ concentration in the solution as a function of the initial molar concentration of the three acids.

$$[H^+]^2 = M_{HNO_3}^0 [H^+] + \frac{M_{HF}^0}{\left(\frac{1}{K_{HF}} + \frac{1}{[H^+]}\right)} + \frac{M_{H_3PO_4}^0}{\left(\frac{1}{K_{H_3PO_4}} + \frac{1}{[H^+]}\right)} + K_w \quad (10)$$

Thus it is possible to calculate the pH of the solution as the negative decimal logarithm of the H^+ molar concentration.

4. pH evaluation as a function of dilution

The pH of the BCP solution as a function of the dilution was estimated using the 3 methods above mentioned:

1. nitric acid concentration,
2. sum of the single effect of each acid,
3. mutual effect of the acids and UPW.

Assuming an initial quantity of 20 ml of acid diluted by steps in up to 500 liter of UPW, the results are shown in table 2 and figure 1.

| UPW vol (liters) | Solution Vol (liters) | 1 Method | 2 Method | 3 Method |
|------------------|-----------------------|----------|----------|----------|
| 1 | 1.02 | 1.12 | 0.94 | 1.01 |
| 5 | 5.02 | 1.81 | 1.51 | 1.57 |
| 10 | 10.02 | 2.11 | 1.75 | 1.83 |
| 50 | 50.02 | 2.80 | 2.32 | 2.39 |
| 100 | 100.02 | 3.11 | 2.57 | 2.61 |
| 200 | 200.02 | 3.41 | 2.84 | 2.89 |
| 300 | 300.02 | 3.58 | 2.99 | 3.05 |
| 400 | 400.02 | 3.71 | 3.11 | 3.18 |
| 500 | 500.02 | 3.81 | 3.20 | 3.26 |

Table 2 pH of BCP (20 ml) diluted in UPW

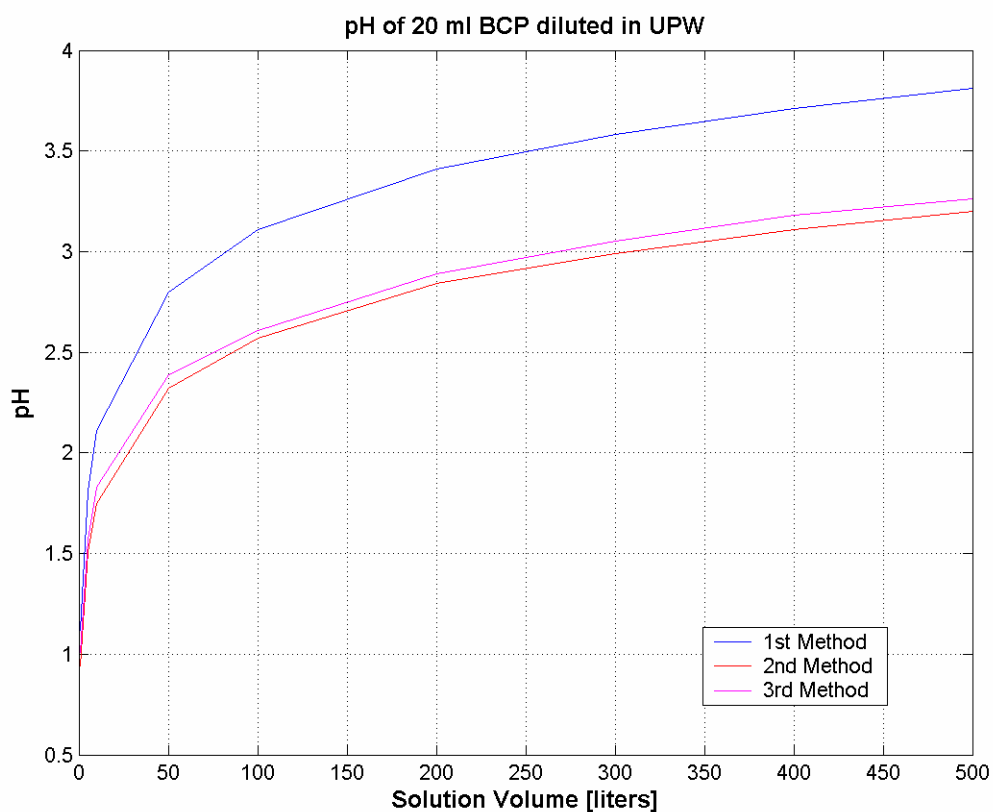


Figure 1 pH of BCP (20 ml) diluted in UPW

One can also calculate the amount of rinses necessary to reach a pH of 7 assuming:

- the initial volume of concentrated BCP: 1, 2, 3, 4, or 5 liters;
- for each rinse the acid is completely mixed and diluted in a 55 gallon barrel of UPW

The results are shown in Figure 2.

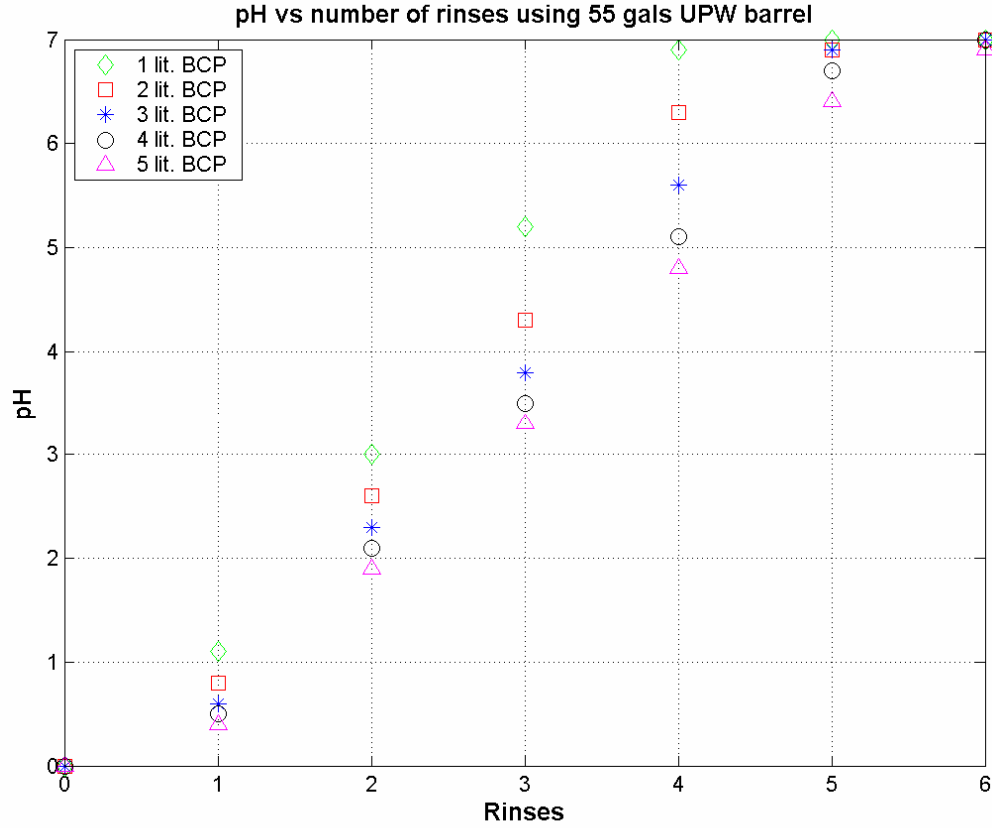


Figure 2 pH as a function of the rinse number

These numbers enable one to estimate the amount of acid remaining in the system after a BCP etching process by measuring the pH of the waste water after each rinse.

5. Resistivity evaluation

The resistivity of the BCP diluted solution can also be calculated. Resistivity, in fact, is the ultimate parameter that one wants to check after a chemical process in order to assure the proper handling of a superconducting cavity. After the final rinse, the water in which the cavity is immersed should have an 18 Mohm-cm resistivity. This value is very close to the theoretical resistivity of water @ 25 C (18.248 Mohm-cm for UPW) and assures that no electrolytic process is ongoing in the solution or between the solution and the niobium cavity. Resistivity is the inverse of conductivity (or specific conductance) [6] which is given by:

$$C = M * \Delta * 1000$$

Where:

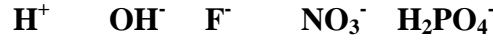
C conductivity in [$\mu\text{S}/\text{cm}$]

M is the molar concentration

Δ is the equivalent conductance [$\text{cm}^2/\text{ohm equivalent}$]

The equivalent conductance is defined as the conductivity of an entire solution containing 1 gram equivalent of solute between electrodes 1 cm apart.

The conductivity of a solution containing multiple electrolytes can be calculated as a sum of the single effects of each species. Assuming (as we did for pH) that the dissociation of H_2PO_4^- to HPO_4^{2-} and to PO_4^{3-} is negligible due to very small equilibrium constants, the electrolytes present in BCP are:



In table 3 are reported the limiting equivalent conductance of these species [7]:

| Electrolyte | Δ [$\text{cm}^2/\text{ohm eq}$] @ 25 C |
|---------------------------|---|
| H^+ | 349.65 |
| OH^- | 198.60 |
| F^- | 55.40 |
| NO_3^- | 71.43 |
| H_2PO_4^- | 33.00 |

Table 3 Limiting equivalent conductance

The hydrogen concentration in the BCP solution is given by equation (10) while the anion concentrations are given by:

$$[\text{NO}_3^-] = M^0_{\text{HNO}_3} \quad (11)$$

$$[\text{F}^-] = \frac{M^0_{\text{HF}}}{\left(1 + \frac{[\text{H}^+]}{K_{\text{HF}}}\right)} \quad (12)$$

$$[\text{H}_2\text{PO}_4^-] = \frac{M^0_{\text{H}_3\text{PO}_4}}{\left(1 + \frac{[\text{H}^+]}{K_{\text{H}_3\text{PO}_4}}\right)} \quad (13)$$

$$[\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} \quad (14)$$

In Figure 3 is shown the correlation between resistivity and pH, while in Figure 4 both resistivity and pH are plotted as a function of the BCP amount dissolved in 2 gallons of UPW.

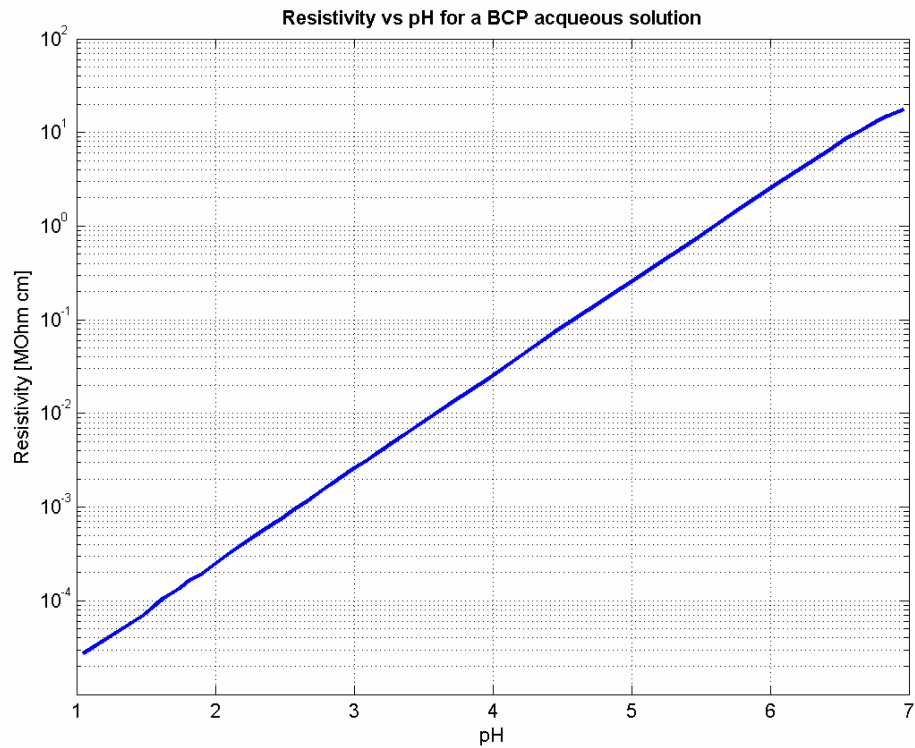


Figure 3 Resistivity versus pH

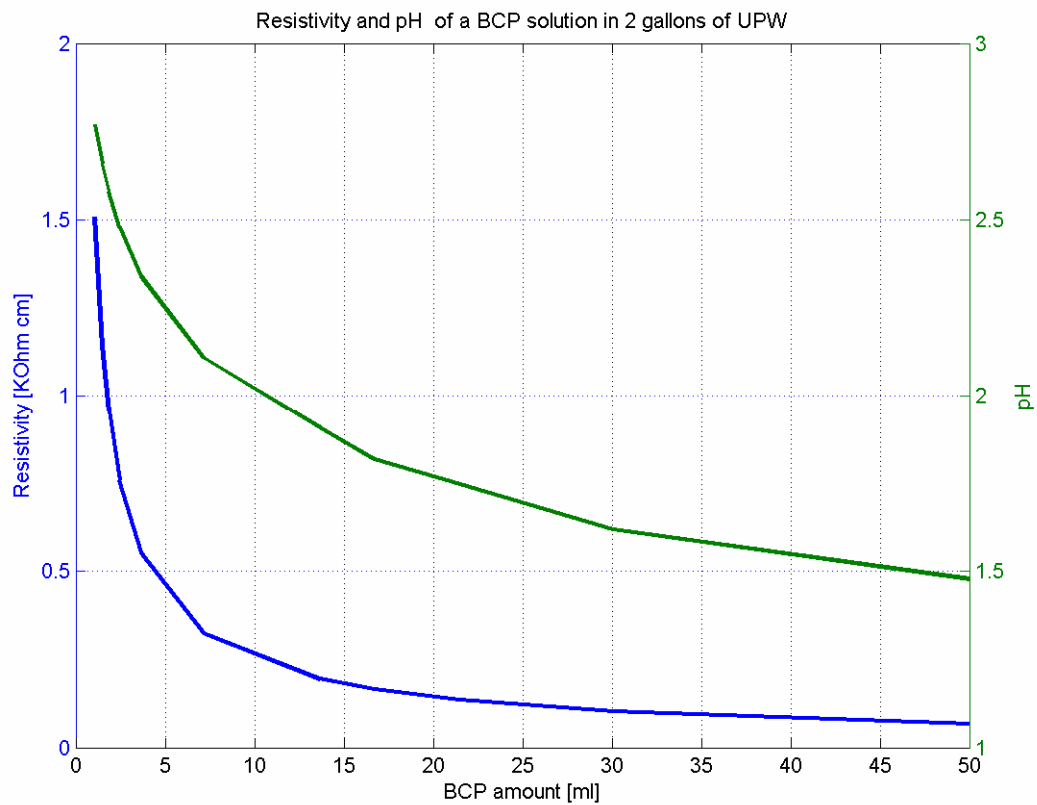


Figure 4 Resistivity and pH vs acid amount in 2 gallons of UPW

The correlation between the acid amount in UPW and pH/resistivity can be used to detect a spill in a tank by adding a known amount of UPW in the secondary container and monitoring the resistivity or pH over time.

6. Comparison with experimental data

In order to confirm the analytical numbers a test was performed by diluting 1 ml of fresh BCP in UPW starting from 50 ml up to 277 liters

6.1. EQUIPMENT:

The measurements were performed using fresh BCP mixed at the TD-MDL and UPW @ 18 MOhm/cm produced by the TD-IB4 UPW system. Three different test strip papers, methyl orange indicator, a conductivity meter and a pH meter were used:

- Panphea paper strips
- Backer paper strips
- EMD paper strips
- GF+ 8850-1 conductivity meter with GF+ transmitter
- GF+ 8750 pH meter with G+ amplifier and transmitter
- The methyl orange indicator changes color from orange to yellow @ pH 4.2

Both the pH and resistivity probes are HF resistant for concentrations below 2%. This constrain limited the initial BCP concentration to 1 ml in 50 ml of UPW. The calibration of the conductivity meter was performed fixing the zero using a buffer solution of pH 4.

6.2. EXPERIMENT

The BCP mix was diluted in several steps up to a total amount of 277 liters. Figure 5 shows the pH versus dilution confirming a good correspondence between the pH meter readings and the analytical value. As expected, the strip papers did not give reliable values in the explored range.

In Figure 6, the measured and calculated correlation between pH and resistivity is shown.

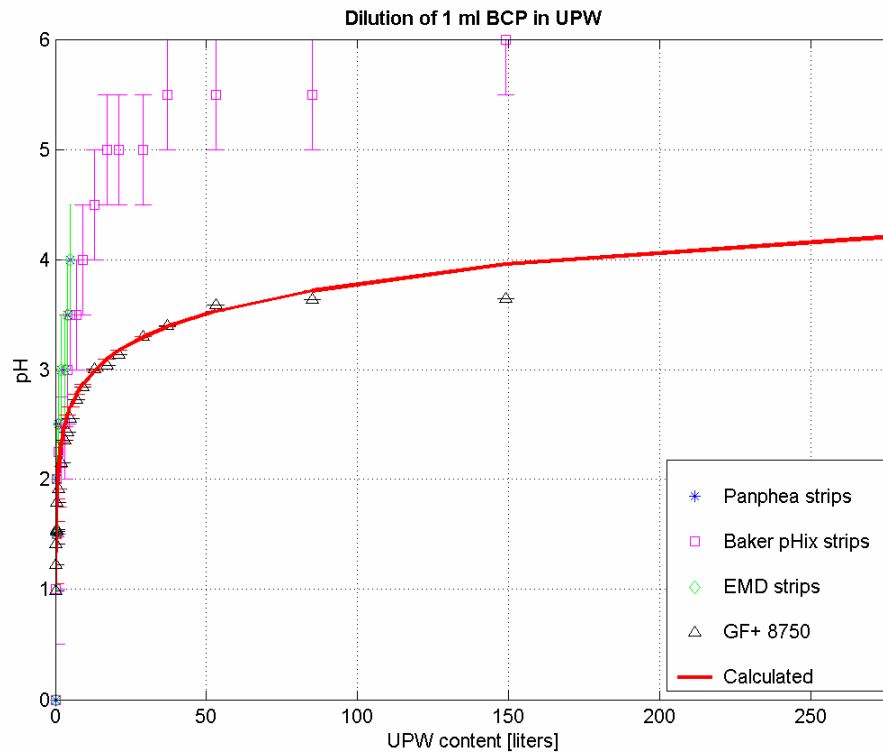


Figure 5 pH of 1 ml BCP diluted in UPW: experimental results and calculation comparison

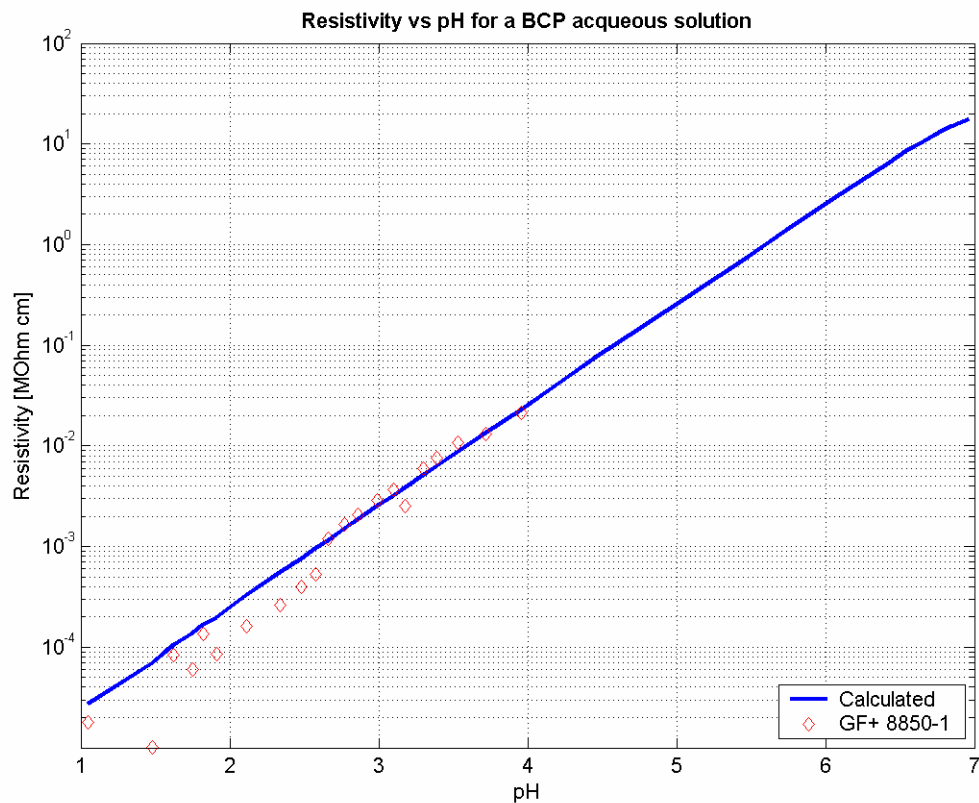


Figure 6 pH vs resistivity of BCP diluted in UPW: experimental results and calculation comparison

7. Conclusions

The purpose of this note is to provide a baseline for the pH and resistivity calculation of diluted BCP mix. Equations for the hydrogen concentration and pH in a BCP solution diluted in UPW and the resistivity were derived and confirmed by experimental data. The results make possible the following solutions for the BCP facility design:

- It is possible to use a resistivity meter as a leak detector in the secondary containment of the acid tanks (gravity feed tank), in the major spill pit, and in the protecting jacket rinsing circuit. As shown in Figure 4, an amount of 1 ml of acid in 2 gallons of UPW changes the water resistivity from 18 Mohm-cm (or probably 1 Mohm-cm after a period of time in which the water is exposed to air and “dirty” plastic surfaces) to around 1.5 kohm-cm, reaching 0.1 kohm-cm when 30 ml of acid is dissolved. The time scale for filling a tank with 50 gallons of acid is around 10 minutes. If the resistivity meter shows a sudden drop in its reading, the system should respond with different actions according to the operational stage. If the leak is reasonably small (around 30 ml in 1 minute) or the filling process is reaching its end, it is possible to let the system finish this stage keeping in mind that acid is present in the secondary containment and probably the main tank needs to be repaired. If the leak is too big and the projection of the total spill amount at the end of the stage is evaluated to be higher than 100 ml, it is necessary to stop the process immediately and dump the acid already present in the tank.
- Leak detection can be also performed with a pH meter. In this case it is possible put in the secondary container a slightly alkaline solution (between pH 7 to 9) and watch for a sudden drop of pH below 7.

Figure 2 allows one to predict the amount of UPW required to perform the initial rinsing of the cavity after etching. The goal of this rinse is to quickly reach at neutral pH in the water in which the cavity is immersed. This operation is performed before routing the cavity to a clean room area where it undergoes a final rinse to reach 18 Mohm-cm. Assuming an amount of 1 to 5 liters of acid trapped in the system and assuming that at each step 55 gallons of UPW are used to rinse the cavity and the pipes of the system, It is possible to predict that 4 to 6 rinses are necessary to reach neutral pH in the water. On another hand, measuring pH during rinsing process and using the results obtained during this study, it will be possible to evaluate the amount of acid trapped in the system

8. References

- [1] H. Padamsee, J. Knobloch, T. Hays, RF Superconductivity for Accelerators, J. Wiley & Sons, New York, 1998
- [2] Y. Terechine et al., BCP Processing Facility, SRF 2003
- [3] MSDS HF
- [4] MSDS HNO₃
- [5] MSDS H₃PO₄

- [6] A. Leveling, The relationship between pH and conductivity in a Lithium Contaminated, De-ionized water system, FNAL Pbar Note 674, June 7, 2002
- [7] Handbook of Chemistry and Physics 78, CRC, 1997-1998